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ABSTRACT

This report describes the technical progress made on the Pittsburgh Air Quality Study (PAQS) during the period of August 2002 through February 2003. The ambient sampling phase of the Pittsburgh Air Quality Study was successfully completed at the end of September 2002. Approximately sixteen months of ambient data have been collected, including three intensive sampling periods (July 2001, January 2002, and July 2002) and several special experiments (instrument intercomparison, nucleation, etc). The structure in Scheneley Park has been removed and the site restored to its original conditions per our agreement with the City of Pittsburgh.

The study average $PM_{2.5}$ mass concentration was approximately $16 \mu g m^{-3}$. Ten high $PM_{2.5}$ mass concentration episodes were experienced at PAQS, several of which were multi-day episodes, and all of which occurred during the warmer summer months. Seasonal variations in $PM_{2.5}$ mass and composition were the result of differences in monthly average organic carbon and sulfate components. Some of the gas-phase, and aerosol measurements were found to exhibit diurnal patterns consistent with diurnal patterns in meteorological measurements. On average, these patterns were not present or not as dramatic in January 2002 as they were in July 2001.

A three-week fence line study adjacent to the largest coke production facility in the United States was conducted this project period. Continuous measurements included meteorological data, CO, SO₂, NO_x, NO, $PM_{2.5}$ mass, and particle size distributions from 3 nm to 1 μm . A combination of meteorological data and pollutant measurements at the fenceline and background sites were used to determine when the coke plant plume was impacting the fenceline site. For example, ratios of SO₂ at the fenceline sampling site to the background site as large as 25 are observed when the fenceline site is in the plume. Semi-continuous measurements of OC/EC (2 hr resolution) and trace metals (30 minute resolution) were made to obtain highly time-resolved composition data. The plume contains greatly elevated OC/EC concentrations; for example, ratios of peak plume OC and EC concentrations to the background site were 18 and 48, respectively. The plume also contains greatly elevated metals concentrations; for example ratios of peak plume Se levels to the background were often greater than a factor of 8.

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INTRODUCTION

This is the fourth semi-annual report of the “Pittsburgh Air Quality Project” (PAQS) funded by the U.S. Department of Energy’s National Energy Technology Laboratory under DOE Cooperative Agreement No. DE-FC26-01NT41017 to Carnegie Mellon University. This work is also supported by the US EPA through the Supersites program. In this three-year project, Carnegie Mellon University will conduct detailed studies of the ambient particulate matter in the Pittsburgh, PA metropolitan area. The work includes ambient monitoring, source characterization, and modeling (statistical and deterministic) for source apportionment. The major objectives of the project include:

- To achieve advanced characterization of the PM in the Pittsburgh region. Measurements include the PM size, surface, volume, and mass distribution; chemical composition as a function of size and on a single particle basis; temporal and spatial variability.
- To obtain accurate current fingerprints of the major primary PM sources in the Pittsburgh region using traditional filter-based sampling and state-of-the-art techniques such as dilution sampling and single particle analysis using mass spectroscopy and LIBS.
- To estimate the impact of the various sources (transportation, power plants, natural, etc.) on the PM concentrations in the area using both statistical and deterministic models.
- To quantify the responses of the PM characteristics to changes in these emissions in support of the emission control decision making in the area.
- To develop and evaluate current and next generation aerosol monitoring techniques for both regulatory applications and for determination of source-receptor relationships.

EXPERIMENTAL

This section provides an overview of the effort on various project activities. This project period the majority of the effort went into Activity 3 Source Characterization and Activity 4 Air Quality Modeling.

Activity 1. Project Management

During this project period a data analysis meeting was held in Charlotte North Carolina in conjunction with the 21st Annual AAAR Conference. The workshop consisted of a whole day of presentations by the PAQS project team describing the status of the research and future plans. The goal of the workshop was to lay the foundation for more integrated analyses that require combining data from multiple investigators. Numerous smaller informal meetings on different topics were also held throughout the week.

The PAQS data management team has been working to submit data to the NARSTO archive, Clarkson University for incorporation in the EPA sponsored relational database, and Advanced Technology Systems for incorporation in the DOE sponsored relational database. The NARSTO format of approximately 80% of July 01 intensive data has been checked by the NARSTO Quality Systems Science Center; several data sets have been checked as many as three times. We are continuing to work on debugging the format. We have initiated transfer of data to Clarkson University for inclusion in EPA sponsored the relational database. Personnel from Advanced Technology Systems also reviewed the data files on the PAQS server.

Activity 2. Ambient Monitoring

The purpose of this activity is to create an extensive database of ambient PM measurements for source apportionment, examination of aerosol processes, evaluation of instrumentation, and air quality model development and evaluation. The ambient sampling phase of the Pittsburgh Air Quality Study was successfully completed at the end of September 2002. Approximately sixteen months of data were collected, including three intensive sampling periods (July 2001, January 2002, and July 2002) and several special experiments (instrument intercomparison, nucleation, etc). The structure in Scheneley Park has been removed and the site restored to its original conditions per our agreement with the City of Pittsburgh.

During September 2002, researchers from Aerodyne (Doug Worsnop and colleagues) together with Jose Jimenez from the University of Colorado at Boulder brought the Aerodyne particle spectrometer to the central site for a two experiment. The major goal of the experiment was to learn more about the composition of the ultrafine particles during nucleation events. Secondary objectives were the inter-comparison of the two particle spectrometers and obtaining additional information about the evolution of the size/composition distribution of the particles. A number of nucleation bursts were observed during the two weeks of this mini-study. Preliminary results suggested that most of the ultrafine particles during these events contained sulfate. This provides significant support to our hypothesis that the initial nuclei consist of sulfate, ammonia, and water and that they grow because of condensation of sulfuric acid and organics. The results from these studies are currently analyzed from all the groups that participated.

The analysis of the collected samples during PAQS should be completed during the next project period. Analyses are complete for OC and EC (three CMU samplers and PC-BOSS), the mass concentrations (FRM, Dichotomous Sampler, and MOUDI impactor). We are almost up-to-date in the analysis of the major inorganic ions (CMU Speciation Sampler, PC-BOSS). There is a small backlog only for the analysis of the metals, the bio-aerosols and the organic speciation (because of the labor-intensive nature of the analysis). Most of the data have been loaded to the PAQS database and are currently undergoing QA/QC.

We are organizing the data to perform the multivariate calibration of the single particle mass spectrometry data. As shown by Fergenson *et al.* (2001), one can use a

combination of bulk particle composition and single particle mass class fraction data to build a calibration model that permits the prediction of the bulk atmospheric aerosol composition from new single particle data. There are several questions we are trying to answer including whether short-term measurements provide more accurate calibration models than long-term samples. Given the hit rate in the mass spectrometer, the shortest time interval we can use is about 6 hours. We can also average the 6 hour data up to 24 hour values to use the 24-hour integrated sample data. We will determine the best approach to developing the most effective calibration model.

Activity 3. Source Characterization

Many primary sources of atmospheric aerosols for the Pittsburgh region are inadequately characterized. The purpose of this activity of this effort is to develop updated emission profiles for important source categories around Pittsburgh.

A three-week fence line study adjacent to the largest coke production facility in the United States was conducted this project period. This is the largest source of emissions in Allegheny County. The measurements were performed at the Allegheny County Health Department Lincoln site. The goal of these measurements is to develop a fingerprint for source apportionment; almost no data are in the published literature for coking facilities. Continuous measurements included: NO_x, SO_x, CO, PM_{2.5} mass, PM_{2.5} OC/EC, PM size distributions, PM_{2.5} metals, and meteorology data. Integrated samples were collected for PM_{2.5} organic speciation, PM_{2.5} ions, VOC concentrations, and PM_{2.5} metals. Preliminary results from this work are described below.

Measurements were performed in the Squirrel Hill Tunnel (a tunnel on Interstate 376 located ~ 2 miles from the central monitoring site) to quantify in-use vehicle emissions in Pittsburgh, Pa. Continuous measurements of CO₂, CO, SO₂, NO_x, NO, PM_{2.5} mass, and particle size distributions from 3 nm to 1 µm were made for a four week period. PM_{2.5} samples were collected and analyzed for organic and elemental carbon (OC/EC), organic composition (speciation), trace metals, and inorganic composition. MOUDIs were collected to determine the mass, OC/EC, and trace metals size distributions. Volatile organic compounds were also measured. Videotapes of traffic were collected for determination of fleet composition and vehicle speed. The sampling focused on three different periods to characterize the effects fleet composition and mode of operation on emissions. The 11 PM to 5 AM period is dominated by fast moving truck traffic (average speed 50 mph, greater than 30% trucks). The 7 to 9 AM period is dominated by slow moving cars (average speed of 20 mph, less than 5% trucks). The 10 AM to 4 PM period is dominated by fast moving cars (average speed of 50 mph, less than 5% trucks).

Preliminary measurements of PM_{2.5} mass and meteorology data were collected at the Allegheny County Health Department North Braddock site that is adjacent to a large steel production facility. The goal of this work is assess the feasibility of conducting a fence line study to characterize a fingerprint for the steel facility.

Collection of road dust was continued during this project period. Samples are being collected from an urban road and a rural road. The collected material will be suspended in a Teflon bag; a PM_{2.5} sample will then be collected from the suspended material for determination of the road dust fingerprint for urban and rural road dust.

The source characterization will continue through the next project period. Goals for the next project period include completion of the database of single particle fingerprints, collection of the road and soil dust sampling, completion of the sampling of vegetative detritus, and stack sampling from a coal-fired power plant. The source sampling has fallen behind the project schedule contained into the proposal because difficulty obtaining permission to sample. We anticipate that the source sampling will be completed by the end of the calendar year 2003.

Activity 4. Source Apportionment

The Hopke group at Clarkson University has begun work on source apportionment. We are working on the development of a factor analysis model that will permit us to utilize data obtained at different sampling frequencies so we do not lose the information contained in the shorter-term values by averaging them back to the longest interval sample. The unique features of the multilinear engine (Paatero, 1999) permit us to build such a model that should permit us to maximally extract source information from the available data.

The Positive Matrix Factorization (PMF) method was applied to the particle size distribution data acquired during the Pittsburgh Air Quality Study (PAQS) from July 2001 to August 2001. After removing those days with nucleation events, a total of 1632 samples each with 165 even-sized intervals from 0.003 to 2.5 micrometers were obtained from Scanning Mobility Particle Spectrometer (SMPS) and Aerodynamic Particle Sizer (APS). The temporal resolution was 15 minutes. The values of each set of five consecutive size bins were summed to produce 33 new size channels. The size distributions of particle number as well as volume were analyzed with a bilinear model. Three kinds of information were used to identify the sources: the number and volume size distributions associated with the factors, the time frequency properties of the contribution of each source (Fourier analysis of source contribution values) and the correlation of the contribution values with the gas-phase data. Through these analyses, the sources were assigned as secondary aerosol, stationary combustion, grown particles and remote traffic, local traffic, and sparse nucleation, in order of increasing number concentration contributions. Conditional probability function (CPF) analysis was performed for each source so as to ascertain the likely directions in which the sources were located. This work has been submitted as a paper for publication (Zhou et al., AS&T, 2003).

Activity 5. Three-Dimensional Deterministic Modeling

During this reporting period the CMU modeling team has continued the development of the aerosol modeling tools, incorporated them in 2 three-dimensional chemical

transport models (URM and CAMx-AERO), and evaluated them against available data sets. Working with the Lake Michigan Air Directors Consortium (LADCO) we have developed preliminary emission inventories for the Eastern United States for the July 2001 intensive (ESP01). Preliminary simulations of the intensive period have been performed with PM-CAMx to evaluate model performance and the emission inventory.

RESULTS AND DISCUSSION

Ambient Monitoring

Daily aerosol measurements collected at the Central Supersite

The study average PM_{2.5} mass concentration was approximately 17 $\mu\text{g m}^{-3}$. Average 24 hour concentrations of mass and the two primary components of the Pittsburgh aerosol (sulfate and organic carbon) are presented in Figure 1. On average, the PM_{2.5} mass concentration was driven by changes in the PM_{2.5} sulfate concentrations.

On ten days, the 24 hour average PM_{2.5} mass concentration was greater than 50 $\mu\text{g m}^{-3}$ at the PAQS central site (August 1, 2, and 9, 2001, June 25 and 26, 2002, and July 1, 2, 8, and 18, 2002). All of the periods occurred during the warmer summer months of 2001 and 2002. Six of the ten periods were actually two-day episodes. These periods and the 24 hour average concentrations experienced during them are listed in Table 1.

Table 1 Peak PM_{2.5} concentrations during PAQS.

Date	Maximum 1 hour mass concentration ($\mu\text{g}/\text{m}^3$)	Average 24 hour mass concentration ($\mu\text{g}/\text{m}^3$)
8/1/01	63.85	55.93
8/2/01	75.08	54.02
8/9/01	72.63	54.22
6/25/02	75.41	56.63
6/26/02	74.28	51.49
7/1/02	76.71	60.94
7/2/02	79.53	56.13
7/8/02	69.31	51.16
7/18/02	70.35	53.37

Seasonal summary of measurements collected at the Central Supersite

Meteorology. The seasonal variations in meteorological variables are shown in Figure 2. Average ambient relative humidity (RH) did not exhibit a strong seasonal dependence and ranged from 60 to 65 percent.

PM₁₀ and PM_{2.5} mass concentrations. Monthly average PM₁₀ mass and PM_{2.5} mass concentrations are presented in Figure 3. On average, approximately 80 percent of the PM₁₀ mass measured at PAQS was in the fine ($< 2.5 \mu\text{m}$) particle range. PM_{2.5} mass measurements obtained using a standard FRM, a Dichot, and a TEOM with sample equilibration were well correlated throughout the study period, as shown in Figure 4, although the TEOM slightly overestimated PM_{2.5} mass. Cabada et al. (2003b) extended this comparison to include MOUDI measurements and found reasonable correlation between the PM_{2.5} mass concentrations measured using the MOUDI and the other integrated sampler measurements.

PM_{2.5} composition. Seasonal differences in the average PM_{2.5} mass composition are presented in Figure 5. Organic matter concentrations for July 2001 are based on 24 hour integrated denuder sampler measurements and the experimentally determined multiplier of 1.8. Organic matter concentrations are based on the difference between the OC collected on the upstream ('bare quartz') and downstream quartz filters of the CMU

TQQQ sampler double-quartz filter pack. Sulfate, nitrate, and ammonium concentrations are composites of measurements made from several methods, including the CMU inorganic sampler, the PC-BOSS, the steam sampler and the Rupprecht and Patashnick 8400 instruments. Crustal component concentrations for August 2001 through June 2002 were estimated from daily July 2001 measurements collected at the PAQS satellite sites to be approximately $1 \mu\text{g m}^{-3}$. Variations in aerosol organic matter, sulfate, and nitrate concentrations are consistent with seasonal variations in ambient temperature and ultraviolet radiation measured at the same location. On average, aerosol organic matter and sulfate concentrations are greatest during the summer months and lowest during the winter months, indicating the importance of photochemical production of these aerosol species. Aerosol nitrate follows the opposite pattern and is lowest during the summer months and greatest during the winter months. Seasonal variations in ultra fine aerosol composition ($< 100 \text{ nm}$), which comprise approximately 5 percent of the total $\text{PM}_{2.5}$ mass, were also observed at the PAQS Supersite. During the summer intensive, Cabada et al. (2003c) found that on average, 55 percent of the ultra fine aerosol mass was inorganic (mainly sulfate and ammonium) and 45 percent of the mass was carbonaceous. During the winter intensive, only 33 percent of the ultra fine aerosol mass was inorganic while 65 percent was carbonaceous in nature.

PM size distributions. Monthly average surface area and volume size distributions are presented in Figure 6. The aerosol surface area distribution was in the fine mode centered at approximately $0.2 \mu\text{m}$ in aerodynamic diameter. The aerosol volume distribution was bimodal, with a majority of the aerosol volume in the fine mode. The two modes were centered at approximately $0.3 \mu\text{m}$ and $3 \mu\text{m}$.

Seasonal differences in diurnal patterns collected at the Central Supersite

Meteorology. Monthly average diurnal profiles were compiled for particular high time resolution measurements for the two intensive periods, July 2001 and January 2002. Diurnal profiles based on several key meteorological measurements are presented in Figure 7 and demonstrate the expected trends.

$\text{PM}_{2.5}$ mass concentration, light scatter, and size distribution. Diurnal profiles for $\text{PM}_{2.5}$ mass concentration and light scattering are presented in Figure 8. Diurnal variations in $\text{PM}_{2.5}$ are not clear when the standard deviation of the hourly average concentrations is also considered. The light scattering by aerosols with diameters less than or equal to 2.5 micrometers exhibits a diurnal pattern that is more clear during July 2001.

Differences in the diurnal profiles of dry and wet particle size and volume distributions for the intensive months are illustrated in Figure 9. The number size distributions exhibit diurnal profiles due to diurnal variations in the smallest mode of particles, with a maximum total number count at midday (Stanier et al., 2003b). The difference between the maximum and minimum number count, is more pronounced in the July 2001 profile, when average ambient $\text{PM}_{2.5}$ concentration was higher. The dramatic difference between the July 2001 ‘dried’ and ‘wet’ (or ambient relative humidity) volume

distributions is the result of high ambient relative humidity and substantial water content of the aerosols.

PM_{2.5} mass composition. Diurnal profiles for particular components of the PM_{2.5} mass were most evident for nitrate and sulfate, as shown in Figure 10. Ambient nitrate exhibited a consistent diurnal pattern throughout the study period, with maximum nitrate observed in the early morning and minimum nitrate observed in the late afternoon (Wittig et al., 2003). The time of the maximum and minimum nitrate shifted with seasonal changes in ambient temperature and UV radiation. Sulfate concentrations varied diurnally only during the summer, consistent with the gas-phase photochemical production during the day. During the summer, maximum sulfate was observed a couple hours before sunset. During the winter, sulfate concentrations were relatively stable over the course of a day. Diurnal profiles for were also evident for PM_{2.5} organic and total carbon, as shown in Figure 11. The features of the profiles varied seasonally, consistent with changes in meteorology.

Gas-phase species. Diurnal profiles for were also evident for several photochemically generated gas-phase species, including O₃, NO, and NO_x, as shown in Figure 12. The features of these particular profiles also varied seasonally. Diurnal variations in CO were not clear when the standard error of the measurements used in the average were also considered.

Key hypothesis-driven findings

This section summarizes the current status of the published hypothesis-driven investigations. These evaluations are based on individual and/or collocated measurements collected at the PAQS Supersite throughout the study period. Detailed experimental work and findings are available in the full reference. Additional work is currently underway to address other hypotheses.

Aerosol mass balance. The monthly average PM_{2.5} concentration for the summer of 2001 was approximately 24 $\mu\text{g m}^{-3}$. Rees et al. (2003) found that there were 24 hour periods during the summer where the sum of the mass of the aerosol chemical components was almost 30 percent less than the mass measured by the FRM. These discrepancies were not as pronounced on a monthly basis. In the 2001 winter months, monthly average PM_{2.5} concentrations were approximately 12 $\mu\text{g m}^{-3}$. During this season, the sum of the mass of the aerosol chemical components was equal to or only slightly below the FRM-measured mass. Rees et al. (2003) explained the mass balance discrepancies of the winter and summer by a combination of factors, including measurement uncertainty, retention of aerosol water, loss of organic material and nitrates, and uncertainty regarding the conversion of organic carbon data to total organic material.

Measurement methods. Subramanian et al. (2003) addressed the organic material sampling artifact issue and found that the measurement of organic material with quartz filters can be prone to both positive and negative sampling artifacts. Several approaches for estimating the sampling artifact were proposed and evaluated, including the use of a

backup quartz filter placed behind either another quartz filter or a Teflon filter or the use of a denuder to reduce the positive artifact in combination with a highly adsorbent backup filter to capture any negative artifact.

A method for semi-continuous PM_{2.5} nitrate and sulfate measurements, based on the humidified impaction with flash volatilization design of Stolzenburg and Hering (2000), was evaluated by Wittig et al. (2003). The accuracy of the semi-continuous measurements was improved by correcting the measurements for several operating parameters. The systematic bias in the corrected semi-continuous measurements was minimized by calibrating the measurements over the entire year using collocated filter-based measurements.

Size spectrometers were found to be a reasonable surrogate for high-time resolution aerosol mass measurements. Khlystov et al. (2003) developed an algorithm to merge aerodynamic particle size distribution measured with an APS and electrical mobility size distribution measured with an SMPS. A comparison of the integrated volume concentration from the merged distributions with the PM_{2.5} mass measured with a TEOM indicates that the size spectrometers merged using the algorithm could be used to estimate PM_{2.5} mass within 20 percent accuracy when the bulk aerosol density was assumed to be 1.5 g cm⁻³.

Secondary organic aerosol production. Ambient secondary organic aerosol (SOA) production was investigated by Cabada et al. (2003b) using the EC tracer method. This method involves the systematic separation of periods where SOA contributes significantly to the ambient OC levels from periods where organic and elemental carbon concentrations are dominated by primary emissions. Ozone is used as an indicator of photochemical activity to identify periods of probable secondary organic aerosol production in the area. Gaseous tracers of combustion sources (CO, NO, and NO_x) are used to confirm periods where most of the OC is primary. Based on this method, Cabada et al. (2003b) estimated that 35 percent of the organic carbon concentration measured at PAQS during the July intensive was secondary in origin.

Gas to particle partitioning of nitrate. Diurnal and seasonal variations in the gas to particle partitioning of nitrate were observed by Wittig et al. (2003). A majority of the nitrate was partitioned into the particle phase at night and into the gas phase during the day. Features of the diurnal patterns and the degree of gas-to-particle partitioning of the nitrate shifted seasonally with temperature, relative humidity, and ultraviolet radiation. During the summer, a majority of the nitrate partitioned into the gas phase during the day, while during winter, little if any nitrate partitioned into the gas phase. Fall and spring showed an intermediate degree of partitioning. When this atmospheric process was modeled using the Gibbs Free-Energy Minimization model (GFEMN) developed by Ansari and Pandis (1999), Takahama et al. (2003) found that the predicted levels of aerosol nitrate were responsive to the temporal resolution of the dominant input variables (T, RH, total ammonium, total nitrate, and total sulfate) when perturbations in the high time resolution variables about the averaged value were small.

Formation of ultra fine particles. Regional nucleation events were investigated by Stanier et al. (2003b). Nucleation events occurred on about 30 percent of the study days, increasing daily averaged number concentration on those days by 40 percent relative to days without nucleation activity. On days with nucleation activity, nucleation was the most important source of particle numbers, similar in strength to local (primarily transportation) emissions. On average, nucleation occurred at around midday, although it occurred earlier in summer and later in winter. It was most frequent in summer and fall, and least frequent in winter. Conditions favorable to nucleation were bright sun and low levels of preexisting aerosols. Evidence from particle mass spectrometers and correlations of nucleation activity with the product of SO₂ and ultraviolet light strongly indicate sulfate as a key component of the new particles. However, published correlations for nucleation by binary H₂SO₄-H₂O can not explain the observed nucleation frequency and intensity, suggesting that an additional component (perhaps ammonia) is participating in the particle formation. Mass spectrometer and hygroscopicity data indicate that organic compounds are also included in the new particles, particularly when they have grown to between 40 nanometers and 100 nanometers in aerodynamic size.

Aerosol water. Stanier et al. (2003a) measured the water content at atmospheric conditions of ambient aerosols between 5 nm and 10 µm in aerodynamic diameter and found that the amount of aerosol water is uncertain over the wide range of relative humidities observed at PAQS. The summer aerosol usually contained water even at relative humidities as low as 30 percent, while the winter aerosol was found to be dry even at relative humidities as high as 60 percent. The spring aerosol showed intermediate behavior. The seasonal difference in water content was attributed to seasonal differences in aerosol acidity, and acidic aerosol conditions were associated with greater water content.

Source Characterization

A three-week fence line study adjacent to the largest coke production facility in the United States was conducted this project period. This is the largest source of emissions in Allegheny County. The measurements were performed at the Allegheny County Health Department Lincoln site. A map showing the sampling site and the coke facility is shown in Figure 13. The sampling site is located at the top of a cliff immediately across the Monongahela River from the coke facility. The site is exposed to the coke plant plume when the wind is blowing from southwest (the predominant wind direction).

Figure 14 plots the ratio of the SO₂ and PM_{2.5} concentrations at the fence line site to the background concentrations as a function of wind direction. The fence line site is downwind of the plant when the wind directions between roughly 180 and 300°. The data indicate a range of pollutant levels when the site is downwind of the plant. During certain periods, pollution levels at the fence line site were more than 25 times higher than the background indicating a strong signal from the coke facility. However, during other periods the pollutant levels at the fence line site are comparable or only slightly elevated relative to background levels even though the site is downwind of the plant; this occurs when the plume is elevated and passes over, but does not directly impact, the fence line

site. The data in Figure 14 underscore the critical need for high time resolution measurements to obtain meaningful emission profiles using fence line sampling.

Figure 15 plots the time series of wind speed and direction, and PM_{2.5} As, Se, OC, and EC measured at the fence line site. The plume contains greatly elevated OC/EC concentrations; for example, ratios of peak plume OC and EC concentrations to the background site were 18 and 48, respectively. The plume also contains greatly elevated metals concentrations; for example ratios of peak plume Se levels to the background were often greater than a factor of 8. Analysis are being performed on data such as those shown in Figure 15 to develop a PM_{2.5} emission profile for the coke facility.

CONCLUSIONS

PAQS is a comprehensive multidisciplinary set of projects in the Pittsburgh region, led by Carnegie Mellon University with contributions by academics, consultants, national laboratories, and state and local air pollution agencies. Measurements were made at a central site, at several satellite sites, and from an aircraft in order to characterize particulate matter (PM) by examination of size, surface area, and volume distribution, chemical composition as a function of size and on a single particle basis, morphology, and temporal and spatial variability in the Pittsburgh region.

The study average PM_{2.5} mass concentration was approximately 16 $\mu\text{g m}^{-3}$. Ten high PM_{2.5} mass concentration episodes were experienced at PAQS, several of which were multi-day episodes, and all of which occurred during the warmer summer months. Seasonal variations in PM_{2.5} mass and composition were the result of differences in monthly average organic carbon and sulfate components. Some of the gas-phase, and aerosol measurements were found to exhibit diurnal patterns consistent with diurnal patterns in meteorological measurements. On average, these patterns were not present or not as dramatic in January 2002 as they were in July 2001.

REFERENCES

- Ansari, A. Pandis, S. N., 1998. On the response of atmospheric particulate matter concentrations to precursor concentrations. *Environmental Science and Technology* (32), 2706-2714.
- Ansari, A. S., Pandis, S. N., 1999. An analysis of four models predicting the partitioning of semivolatile inorganic aerosol components. *Aerosol Science and Technology* 31, 129-153.
- Blando, J. D., Porcja, R. J., Turpin, B. J., 2001. Issues in the quantitation of functional groups by FTIR spectroscopic analysis of impactor-collected aerosol samples. *Aerosol Science and Technology* (35), 899-908.

Cabada, J. C., Khlystov, A., Wittig, B., Pandis, S. N., 2003a. Fine particle light scattering reconstruction and measurements at PAQS. Submitted to Atmospheric Environment.

Cabada, J. C., Pandis, S. N., Subramanian, R., Robinson, A. L., Polidori, A., Turpin, B., 2003b. Estimating the secondary organic aerosol contribution to PM_{2.5} using the EC tracer method. Submitted to Atmospheric Environment.

Cabada, J. C., Takahama, S., Khlystov, A., Pandis, S. N., Rees, S., Davidson, C. I., Robinson, A. L., 2003c. Mass size distributions and size resolved chemical composition of fine particulate matter at the Pittsburgh Supersite. Submitted to Atmospheric Environment.

Carson, P.G., Johnston, M.V., Wexler, A.S., 1997. Laser desorption ionization of ultra fine aerosol particles. *Rapid Communications of Mass Spectroscopy* (11), 993-996.

Demoz, B., Collett, Jr., J. L. Daube, Jr., B. C. , 1996. On the Caltech Active Strand Cloudwater Collectors. *Atmospheric Research* (41), 47-62.

Eatough, D. J., Eatough, N. L., Obeidi, F., Pang, Y., Modey, W., Long, R., 2001. Continuous determination of PM_{2.5} mass, including semi-volatile species. *Aerosol Science and Technology* (34), 1-8.

Ferguson, D.P. , X.-H. Song, Z. Ramadan, J.O. Allen, L.S. Hughes, G.R. Cass, P.K. Hopke and K.A. Prather (2001), The Quantification of ATOFMS Data by Multivariate Methods, *Anal. Chem.* 73: 3535-3541.

Ge, Z., Wexler, A.S., Johnston, M.V., 1998. Laser desorption/ionization of single ultra fine multicomponent aerosols. *Environmental Science and Technology* (32), 3218-3223.

Harris, J.M. Kahl, J.D.W., 1994. An analysis of 10-day isentropic flow patterns for Barrow, Alaska: 1985-1992. *Journal of Geophysical Research* (99), 25845-25955.

Jaffrezo, J. L., Calas, T., Bouchet, M., 1998. Carboxylic acids measurements with ionic chromatography. *Atmospheric Environment* (32), 2705-2708.

Jayne, J. T., Leard, D. C., Zhang, X., Davidovits, P., Smith, K. A., Kolb, C. E., Worsnop, D. R., 2000. Development of an aerosol mass spectrometer for size and composition analysis of submicron particles. *Aerosol Science and Technology* (33), 49-70.

Khlystov, A., Wyers, G. P., Slanina, J., 1995. The steam-jet aerosol collector. *Atmospheric Environment* (29), 2229-2234.

Khlystov, A., Wittig, B., Davidson, C., 2001. Quality Assurance Project Plan For The Pittsburgh Air Quality Study. Report Prepared For The U. S. E. P. A., Research Triangle Park, Nc.

Khlystov, A., Stanier, C., Pandis, S.N., 2003. An algorithm for combining electrical mobility and aerodynamic size distributions data when measuring ambient aerosol. Submitted to Aerosol Science and Technology.

Kidwell, C. B., Ondov, J. M., 2001. Development and evaluation of a prototype system for collecting sub-hourly ambient aerosol for chemical analysis. Aerosol Science and Technology (35), 596-601.

Lazrus, A. L., Kok, G. L., Lind, J. A., Gitlin, S. N., Heikes, B. G., Shetter, R. E., 1986. Automated fluorometric method for hydrogen peroxide in air. Analytical Chemistry (58), 594-597.

Lewis, C. W., Stevens, R. K., Rasmussen, R. A., Caldelino, C. A., Pierce, T. E., 1999. Biogenic fraction of ambient VOC: Comparison of radiocarbon, chromatographic, and emission inventory estimates for Atlanta, Georgia. Journal of the Air and Waste Management Association (49), 299-307.

MSP Corp., Inc., 1998. Operator's Manual for the Micro-Orifice Uniform Deposit Impactor. Shoreview, MN.

NIOSH, 1996. Elemental carbon (diesel exhaust). In: NIOSH Manual of Analytical Methods. National Institute of Occupational Safety and Health, Cincinnati, OH.

Paatero, P., 1999. The Multilinear Engine --- a Table-driven Least Squares Program for Solving Multilinear Problems, Including the n-way Parallel Factor Analysis Model. Journal of Computational and Graphical Statistics 8, 854-888

Rees, S. L., Robinson, A. L., Khlystov, A., Stanier, C. O., Subramanian, R., Cabada, J. C., Wittig, B., Takahama, S., Davidson, C., Pandis, S., 2003. Mass balance closure and the Federal Reference Method for PM_{2.5} in Pittsburgh, PA. Submitted to Atmospheric Environment.

Slanina, J., ten Brink, H. M., Otjes, R. P., Even, A., Jongejan, P., Khlystov, A., Waijers-Ijpelaan, A., Hu, M., 2001. The continuous analysis of nitrate and ammonium in aerosols by the Steam Jet Aerosol Collector (SJAC): Extension and validation of the methodology. Atmospheric Environment (35), 2319-2330.

Stanier, C. O., Khlystov, A., Chan, R., Mandiro, M., Pandis, S. N., 2003a. A method for the in-situ measurement of fine aerosol water content of ambient aerosols: The Dry-Ambient Aerosol Size Spectrometer (DAASS). Accepted by Aerosol Science and Technology.

Stanier, C. O., Khlystov, A., Pandis, S. N., 2003b. Nucleation events during the Pittsburgh Air Quality Study: Description and relation to key meteorological, gas-phase, and aerosol parameters. Accepted by Aerosol Science and Technology.

Stolzenburg, M. R. Hering, S. V., 2000. A new method for the automated measurement of atmospheric fine particle nitrate. *Environmental Science and Technology* (34), 907-914.

Subramanian, R., Khlystov, A., Y., Cabada, J. C., Robinson, A. L., 2003. Positive and negative artifacts in particulate organic carbon measurements with denuded and undenuded sampler configurations. Submitted to *Aerosol Science and Technology*.

Takahama, S., Khlystov, A., Wittig, B., Davidson, C., Pandis, S. N., 2003. Partitioning of nitrate during the Pittsburgh Air Quality Study and implications of time-averaging. Submitted to *Atmospheric Environment*.

Thermo Andersen, 1999. Operator's Manual for PM₁₀ High Volume Sampler. Smyrna, GA.

Turpin, B. J., Cary, R. A., Huntzicker, J. J., 1990. An in-situ time-resolved analyzer for aerosol organic and elemental carbon. *Aerosol Science and Technology* (12), 161-171.

USEPA, 1991. EPA Method 200.8 (rev 4.4): Determination of trace elements in waters and wastes by Inductively Coupled Plasma – Mass Spectrometry. Research Triangle Park, NC.

USEPA, 1994. EPA Method 6020: Inductively Coupled Plasma Mass Spectrometry. Research Triangle Park, NC.

USEPA, 1998. EPA Quality assurance guidance 2.12: Monitoring PM_{2.5} in ambient air using designated references or Class I equivalence methods. Research Triangle Park, NC.

USEPA, 1999. EPA Method 625 (rev R-96/01a): Compendium of methods for the determination of inorganic compounds in ambient air. Research Triangle Park, NC.

Wittig, B., Takahama, S., Khlystov, A., Pandis, S. N., Hering, S., Kirby, B., Davidson, C., 2003. Semi-continuous PM_{2.5} inorganic composition measurements during the Pittsburgh Air Quality Study. Submitted to *Atmospheric Environment*.

PRESENTATIONS AND PUBLICATIONS

1. J. C. Cabada, S. N. Pandis, and A. L. Robinson (2002) Sources of atmospheric particulate matter in Pittsburgh, Pennsylvania, *JAWMA*, 52, 732-741.
2. C. O. Stanier, A. Khlystov, and S. N. Pandis (2002) Chemical processes and long-range transport of aerosols: Insights from the Pittsburgh Air Quality Study, in *Long Range Transport of Air Pollution*, Kluwer.

3. Subramanian R., A. Y. Khlystov, J. C. Cabada-Amaya, and A. L. Robinson (2003) Sampling artifacts during measurement of ambient carbonaceous aerosol, *Aerosol Sci. Technol.*, (submitted).
4. Cabada J. C., S. N. Pandis, A. L. Robinson, R. Subramanian, A. Polidori, and B. Turpin (2003) Estimating the secondary organic aerosol contribution to PM_{2.5} using the EC tracer method, *Aerosol Sci. Technol.*, (submitted).
5. Stanier C. O., A. Y. Khlystov, and S. N. Pandis (2003a) Nucleation events during the Pittsburgh Air Quality Study: Description and relation to key meteorological, gas phase, and aerosol parameters, *Aerosol Sci. Technol.*, (submitted).
6. Stanier C. O., A. Khlystov, W. R. Chan, M. Mandiro, and S. N. Pandis (2003b) A method for the in-situ measurement of aerosol water content of ambient aerosols: The Dry Ambient Aerosol Size Spectrometer (DAASS), *Aerosol Sci. Technol.*, (submitted).
7. A. Khlystov, C. O. Stanier, and S. N. Pandis (2003) Aerosol size distribution measurements from 3 nm to 10 μ m: Instrument performance and particle properties, *Aerosol Sci. Technol.*, (submitted).
8. Zhou L. and P. Hopke (2003) The Advanced Factor Analysis on Pittsburgh particle size distribution data, *Aerosol Sci. Technol.*, (submitted).
9. Rees S. L., A. L. Robinson, A. Khlystov, C. O. Stanier, and S. N. Pandis (2003) The PM_{2.5} Federal Reference Method (FRM) and the chemical mass balance for fine particulate matter, *Aerosol Sci. Technol.*, (in preparation).
10. Wittig B., A. Y. Khlystov, S. Takahama, S. N. Pandis, S. Hering, B. Kirby, and C. Davidson (2003) Semi-continuous PM_{2.5} inorganic composition measurements during the Pittsburgh Air Quality Study, *Atmos. Environ.* (submitted).
11. Subramanian R. , A. Y. Khlystov, B. J. Turpin, A. L. Robinson (2003) Measurement of Ambient Carbonaceous Aerosols During the Pittsburgh Air Quality Study, *Atmos. Environ.* (in preparation).
12. Khlystov A. Y., C. O. Stanier, and S. N. Pandis (2003) In-situ continuous PM water concentrations measurements, *Atmos. Environ.*, (in preparation).

13. Stanier C. O., A. Y. Khlystov, and S. N. Pandis (2003) Aerosol size distribution climatology, *Atmos. Environ.* (in preparation).
14. Cabada J. C., S. Rees, S. Takahama, A. Y. Khlystov, W. Tang, C. Davidson, and S. N. Pandis (2003) Aerosol size-composition distributions during PAQS, *Atmos. Environ.*, (in preparation).
15. Vayenas D., S. Takahama, and S. N. Pandis (2003) Formation and removal of ammonium nitrate and its precursors: System responses to emission changes, *Atmos. Environ.*, (in preparation).
16. Takahama S., D. Vayenas, S. N. Pandis, and C. Davidson (2003) Evaluating the aerosol equilibrium assumption in an urban area in the Northeastern US, *Atmos. Environ.*, (in preparation).
17. Eatough D. and C. Davidson (2003) Meteorological influence on, and diurnal patterns in ambient fine particulate chemical composition at two sampling sites in metropolitan Pittsburgh: A 2001 intensive summer study, *Atmos. Environ.*, (in preparation).
18. Eatough D. and C. Davidson (2003) Source apportionment of PM_{2.5}, organic material and sulfate during the July 2001 summer intensive, *Atmos. Environ.*, (in preparation).
19. Gaffney J. et al. (2003) Natural radionuclides in fine aerosols in Pittsburgh, *Atmos. Environ.*, (in preparation).
20. Rogge W. et al. (2003) Organic PM_{2.5} at the Pittsburgh Supersite: Regional versus local concentrations and seasonal variations, *Atmos. Environ.*, (in preparation).
21. Cabada J. C., A. Khlystov, B. Wittig, and S. N. Pandis (2003) Fine particle light scattering reconstruction and measurements at PAQS, *Atmos. Environ.* (in preparation).

Presentations:

1. "Investigation of nucleation bursts in the Pittsburgh air quality study", 6th International Aerosol Conference, Taipei, Taiwan, September 2002 (C. O. Stanier, A. Y. Khlystov, and S. N. Pandis).

2. "Monitoring of water content of ambient aerosol during the Pittsburgh Air Quality Study" 6th International Aerosol Conference, Taipei, Taiwan, September 2002 (A. Y. Khlystov, C. O. Stanier, D. Vayenas, and S. N. Pandis).
3. Performance of the Aerodynamic Particle Sizer 3320 during the Pittsburgh Air Quality Study (PAQS)" 6th International Aerosol Conference, Taipei, Taiwan, September 2002 (A. Khlystov, C. Stanier, and S. N. Pandis).
4. "Sulfate-ammonia-nitric acid interactions in an urban area" 6th International Aerosol Conference, Taipei, Taiwan, September 2002 (S. Takahama, A. Khlystov, B. Wittig, S. V. Hering, C. Davidson, A. Robinson, and S. N. Pandis).
5. "Sampling artifacts during measurement of ambient carbonaceous aerosol" 6th International Aerosol Conference, Taipei, Taiwan, September 2002 (R. Subramanian, A. Y. Khlystov, J. C. Cabada, S. N. Pandis, and A. L. Robinson).
6. "Formation and properties of regional aerosol: Some insights from the Pittsburgh Air Quality Study", NASA-GSFC, Greenbelt MD, May 2002,(C. Stanier, A. Khlystov, S. Rees, J. Cabada, A. Robinson, C. Davidson, and S. N. Pandis)
7. "Seasonal composition of PM_{2.5} and performance of the Federal Reference Method in Pittsburgh", PM_{2.5} and Electric Power Generation, Pittsburgh, April 2002 (S. L. Rees, S. Takahama, A. L. Robinson, A. Khlystov, and S. N. Pandis).
8. "Continuous measurements of ammonia, sulfate, and nitrate in Pittsburgh: Implications for PM_{2.5} control strategies", PM_{2.5} and Electric Power Generation, Pittsburgh, April 2002 (B. Wittig, A. Khlystov, S. Takahama, C. Davidson, A. Robinson, S. Hering, and S. N. Pandis).
9. "The contribution of long-range transport and secondary organic aerosol to PM_{2.5} in Pittsburgh", PM_{2.5} and Electric Power Generation, Pittsburgh, April 2002 (J. C. Cabada, R. Subramanian, S. N. Pandis, A. L. Robinson, W. Tang, N. J. Anderson, T. Raymond, and C. I. Davidson).
10. "The Dry-Ambient Size Spectrometer: A new technique for the automatic on-line measurement of the atmospheric aerosol water size distribution", Annual Meeting of American Geophysical Union, San Francisco, December 2001 (A. Khlystov, C. O. Stanier, S. N. Pandis).

11. “The July 2001 intensive of the Pittsburgh Air Quality Study”, Annual Meeting of AAAR, Portland, Oregon, October 2001 (C. I. Davidson, A. L. Robinson, and A. Khlystov, S. N. Pandis).
12. “Sources of atmospheric carbonaceous particulate matter in Pittsburgh”, Annual Meeting of AAAR, Portland, Oregon, October 2001 (J. Cabada, S. N. Pandis and A. L. Robinson).
13. “Automated measurements of dry and wet ambient aerosol distributions”, Annual Meeting of AAAR, Portland, Oregon, October 2001 (A. Y. Khlystov, W. R. Chan, C. O. Stanier, M. Mandiro, and S. N. Pandis)
14. “Continuous measurements of ammonia and ammonium in ambient air”, Annual Meeting of AAAR, Portland, Oregon, October 2001 (A. Khlystov, J. Sauser, R. Otjes, and S. N. Pandis).
15. The contribution of secondary organic aerosol to PM_{2.5} concentrations in Pittsburgh, AGU Fall Meeting 2002, San Francisco CA Dec. 2002 (J. C. Cabada, S. N. Pandis, A. L. Robinson, R. Subramanian, A. Polidori, and B. Turpin).
16. Preliminary results from the Pittsburgh Air Quality Study, AGU Fall Meeting 2002, San Francisco CA Dec. 2002 (S. N. Pandis, C. I. Davidson, A. L. Robinson, and A. Y. Khlystov)
17. Monitoring of water content of ambient aerosol during the Pittsburgh Air Quality Study, AGU Fall Meeting 2002, San Francisco CA Dec. 2002 (A. Y. Khlystov, C. O. Stanier, D. Vayenas, and S. N. Pandis)
18. Investigation of nucleation bursts during the Pittsburgh Air Quality Study, AGU Fall Meeting 2002, San Francisco CA Dec. 2002 (C. O. Stanier, A. Y. Khlystov, B. Wittig, S. N. Pandis, Y. Zhou, K. Bein, A. S. Wexler, C. Misra, and C. Sioutas)

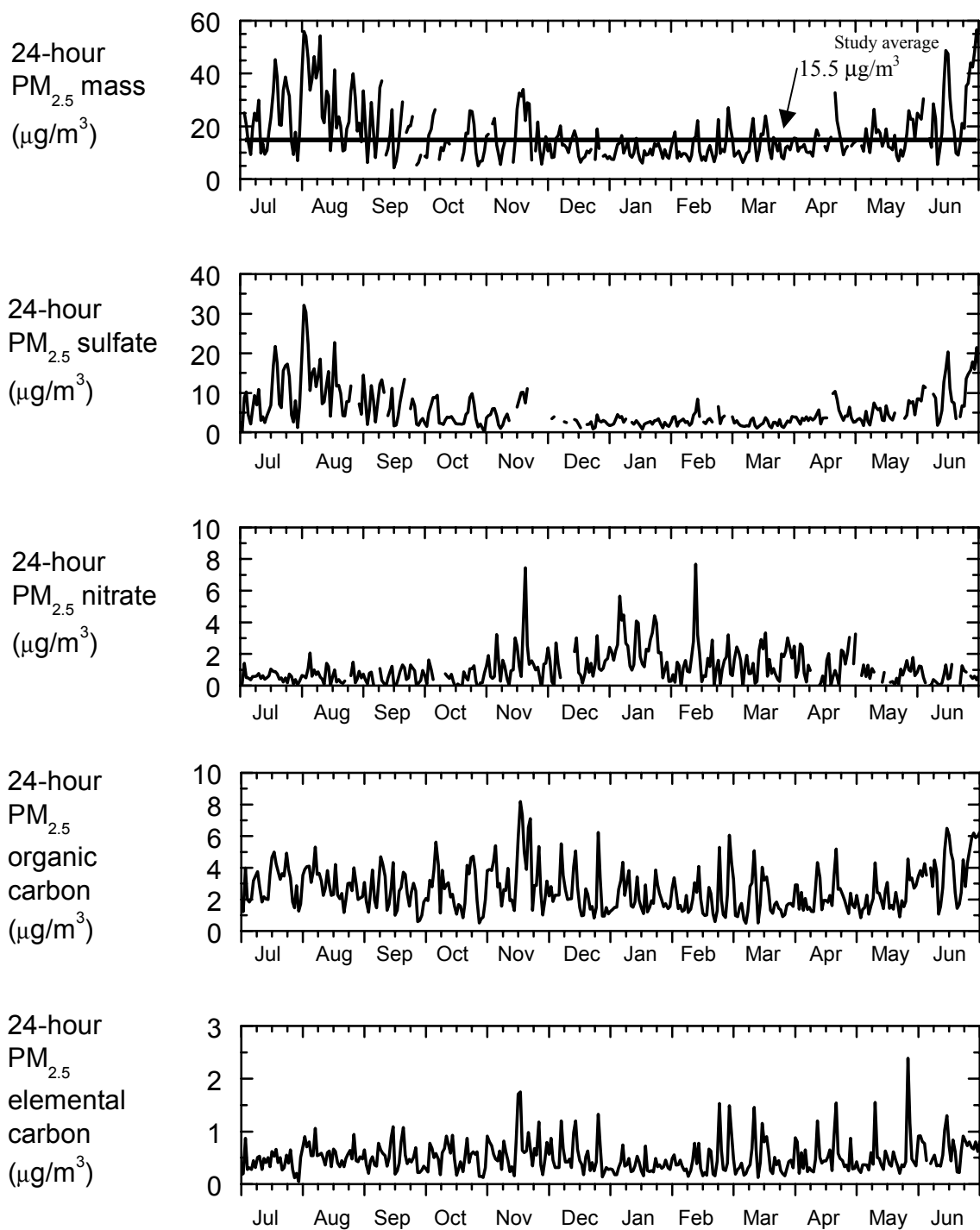


Figure 1. Daily 24 hour average mass, sulfate, nitrate, organic carbon, and elemental carbon concentrations at the PAQS Supersite from July 2001 to June 2002.

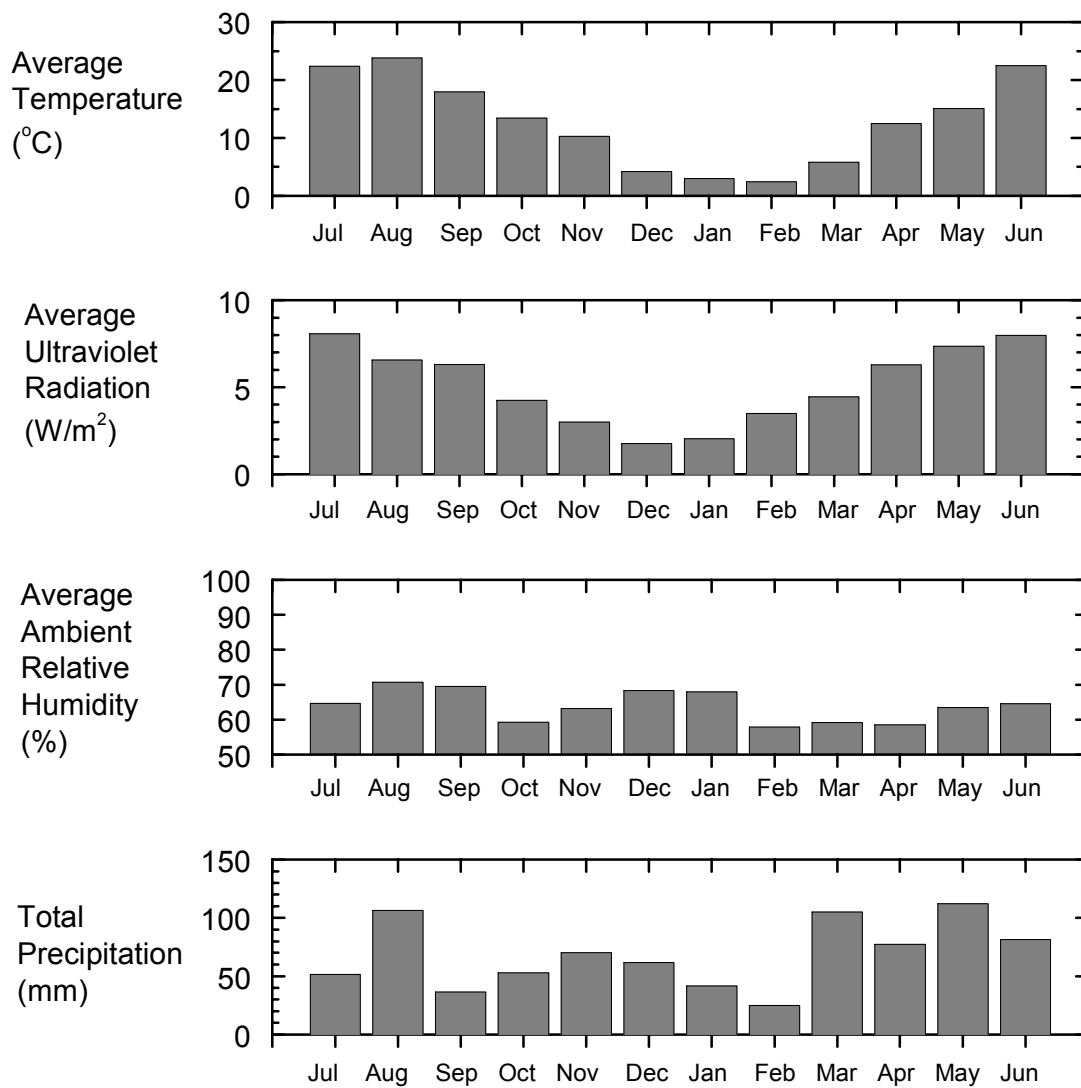


Figure 2. Monthly average ambient temperature, ultraviolet radiation, and relative humidity, and monthly total precipitation measured at the PAQS Supersite from July 2001 to June 2002.

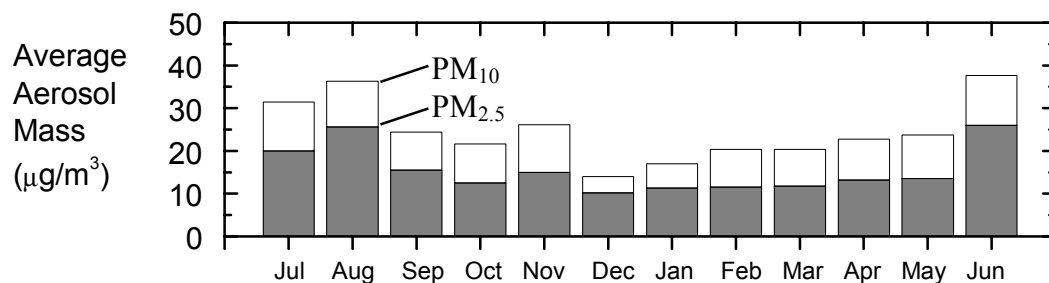


Figure 3. Monthly average PM₁₀ mass and PM_{2.5} mass measured at the PAQS Supersite from July 2001 to June 2002. PM₁₀ mass was measured on a 24 hour basis using a standard Dichotomous (Dichot) sampler, while PM_{2.5} mass was measured on a 24 hour basis using a standard Federal Reference Method (FRM) sampler.

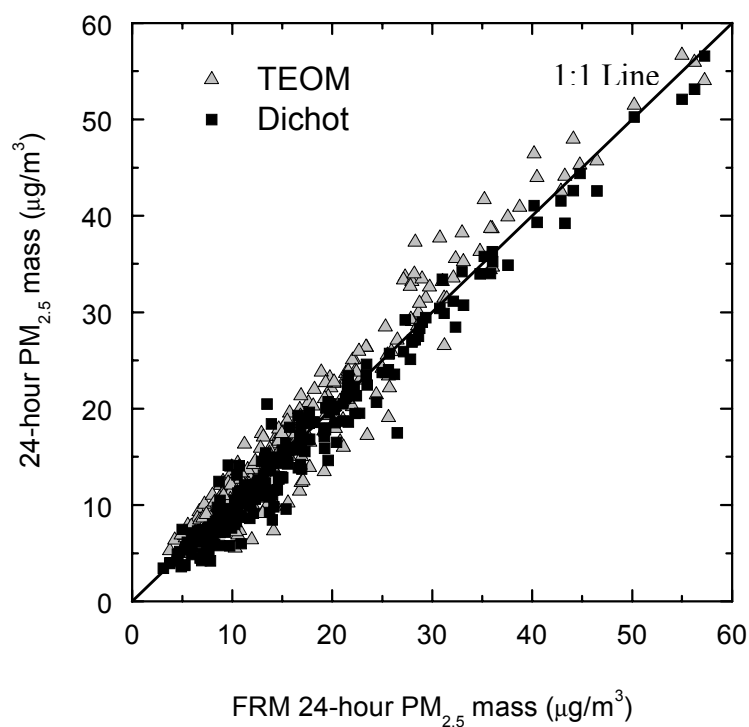


Figure 4. Comparison of 24-hour integrated FRM PM_{2.5} mass measurements and other PM_{2.5} mass measurements collected at the PAQS Supersite from July 1, 2001 to June 30, 2002. Integrated Dichot measurements were collected on a daily basis, while TEOM measurements were collected continuously and averaged on a 24 hour basis.

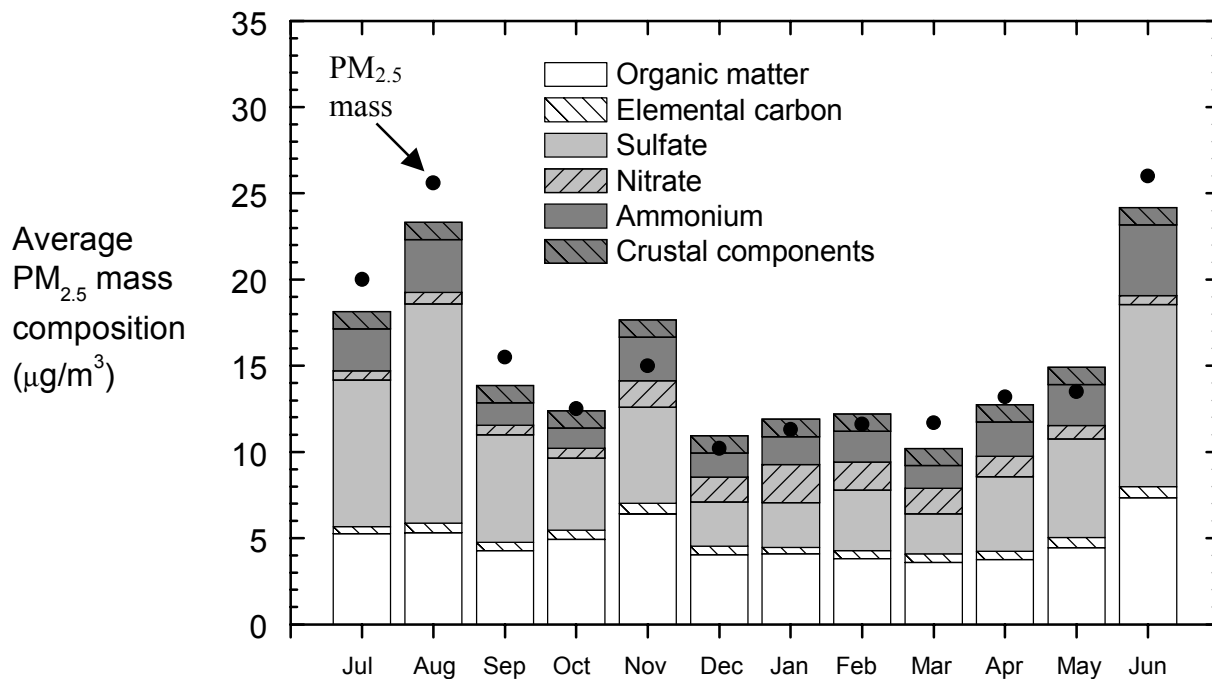


Figure 5. $PM_{2.5}$ composition on a monthly average basis at the PAQS Supersite from July 2001 to June 2002. Also shown is the $PM_{2.5}$ total mass measured using the FRM. Organic matter concentrations for July 2001 are based on 24 hour integrated denuder sampler measurements and the experimentally determined multiplier of 1.8. Organic matter concentrations are based on the difference between the OC collected on the upstream ('bare quartz') and downstream quartz filters of the CMU TQQQ sampler double-quartz filter pack. Sulfate, nitrate, and ammonium concentrations are composites of measurements made from several methods, including the CMU inorganic sampler, the PC-BOSS, the steam sampler and the Rupprecht and Patashnick 8400 instruments. Crustal component concentrations for August 2001 through June 2002 were estimated from daily July 2001 measurements collected at the PAQS satellite sites to be approximately $1 \mu\text{g m}^{-3}$.

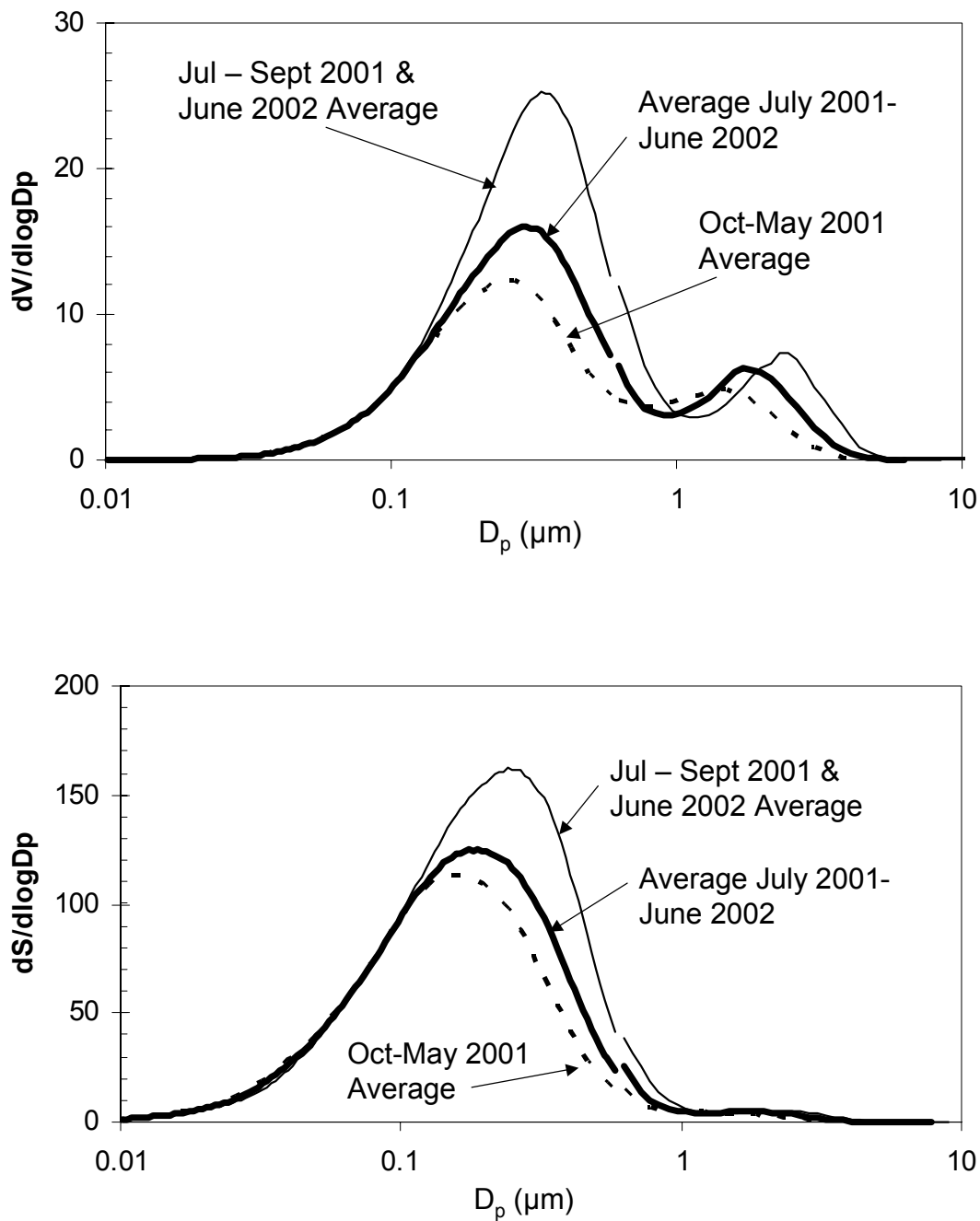


Figure 6. Aerosol surface area and volume size distributions composition on a monthly average basis at the PAQS Supersite from June 2001 to May 2002. Units for the surface area distribution are $\mu\text{m}^2/\text{cm}^3$; units for the volume distribution are $\mu\text{m}^3/\text{cm}^3$.

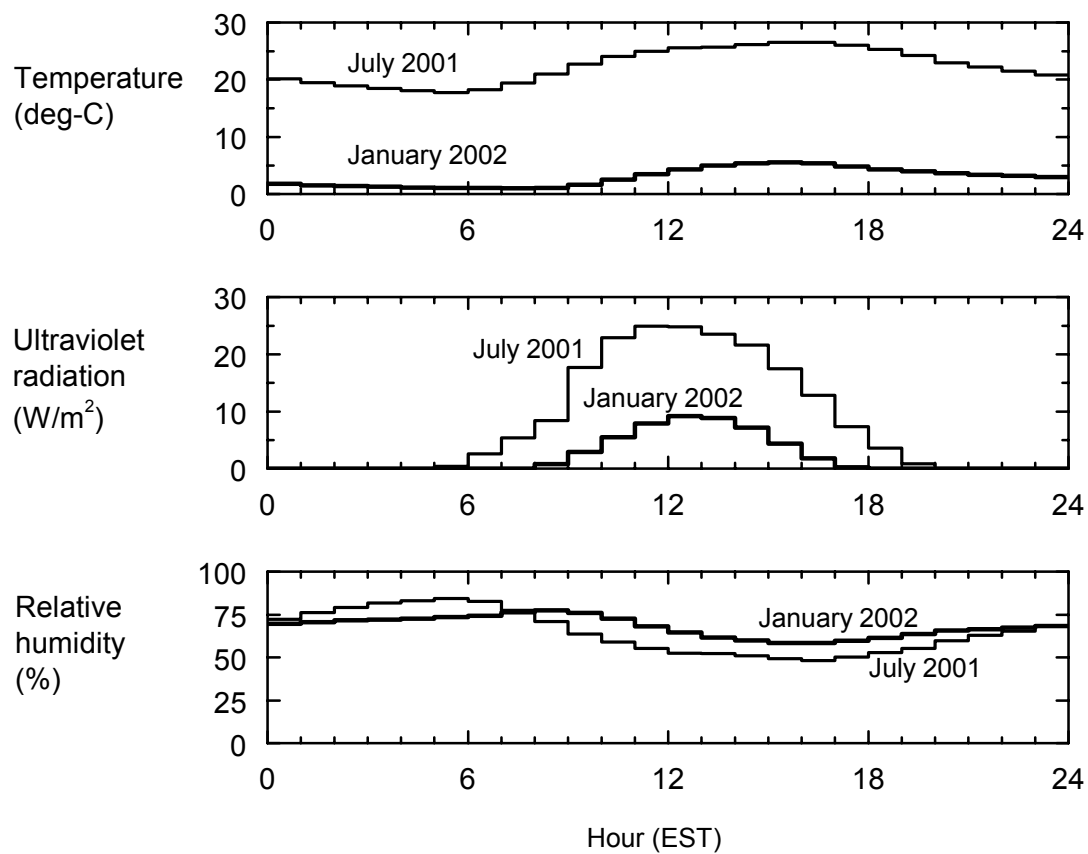


Figure 7. Diurnal variation in ambient temperature, ultraviolet radiation, and relative humidity for July 2001 and January 2002 at the PAQS Supersite.

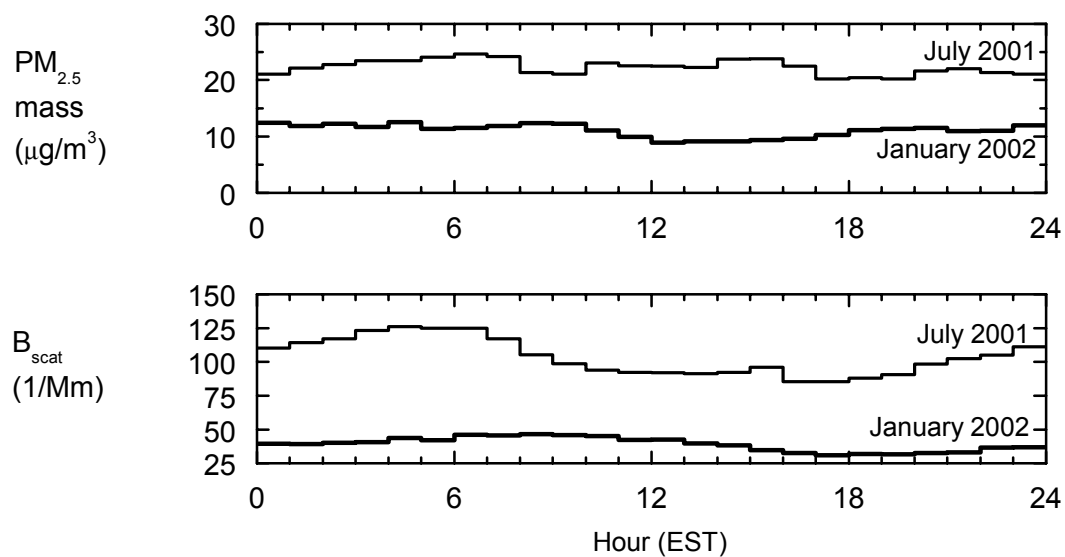


Figure 8. Diurnal variation in PM_{2.5} mass and back scatter for July 2001 and January 2002 at the PAQS Supersite. PM_{2.5} mass was measured using a 30-degree Celsius TEOM with SES and back scatter was measured using an ambient temperature Optec NGN3 nephelometer.

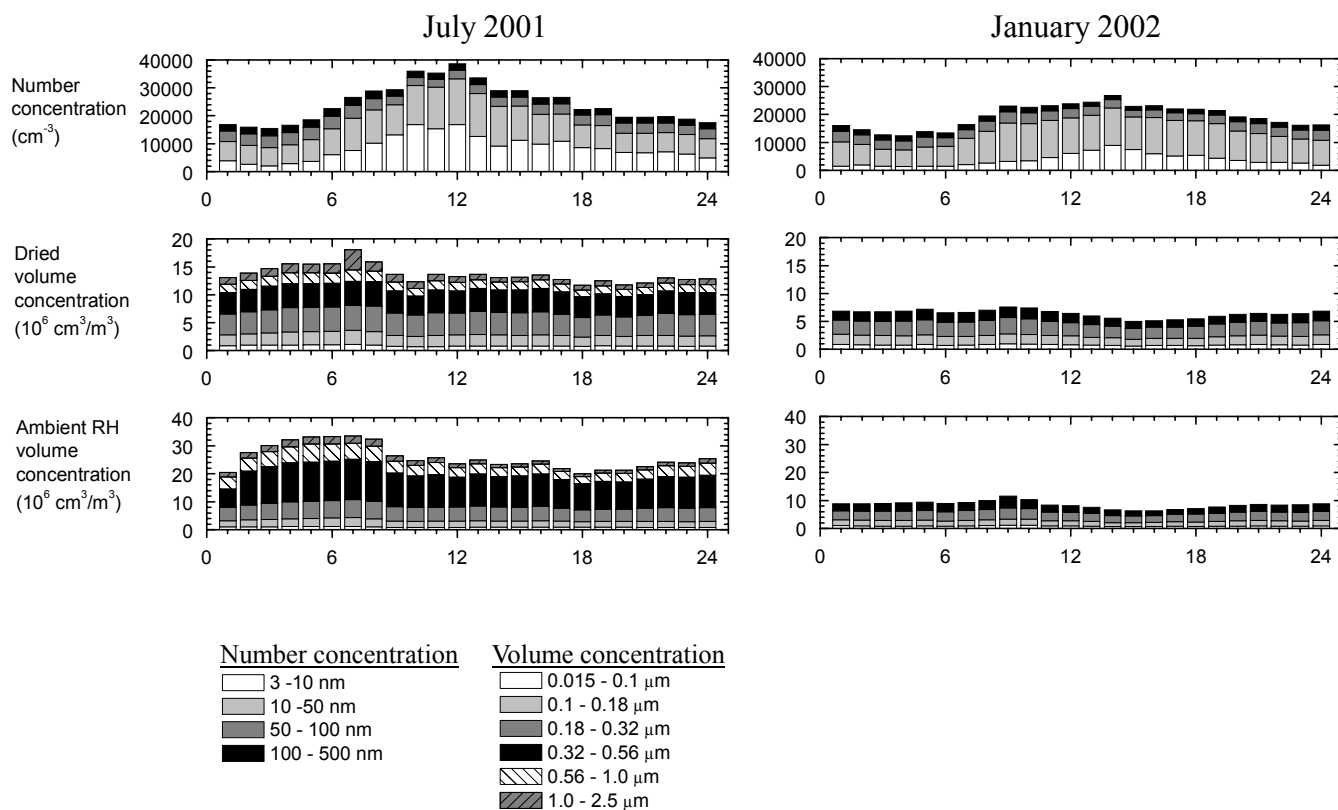


Figure 9. Diurnal variation in size distribution for July 2001 and January 2002 at the PAQS Supersite. The size distributions were measured using a suite of particle sizing instruments, including a nano-SMPS, SMPS, and APS.

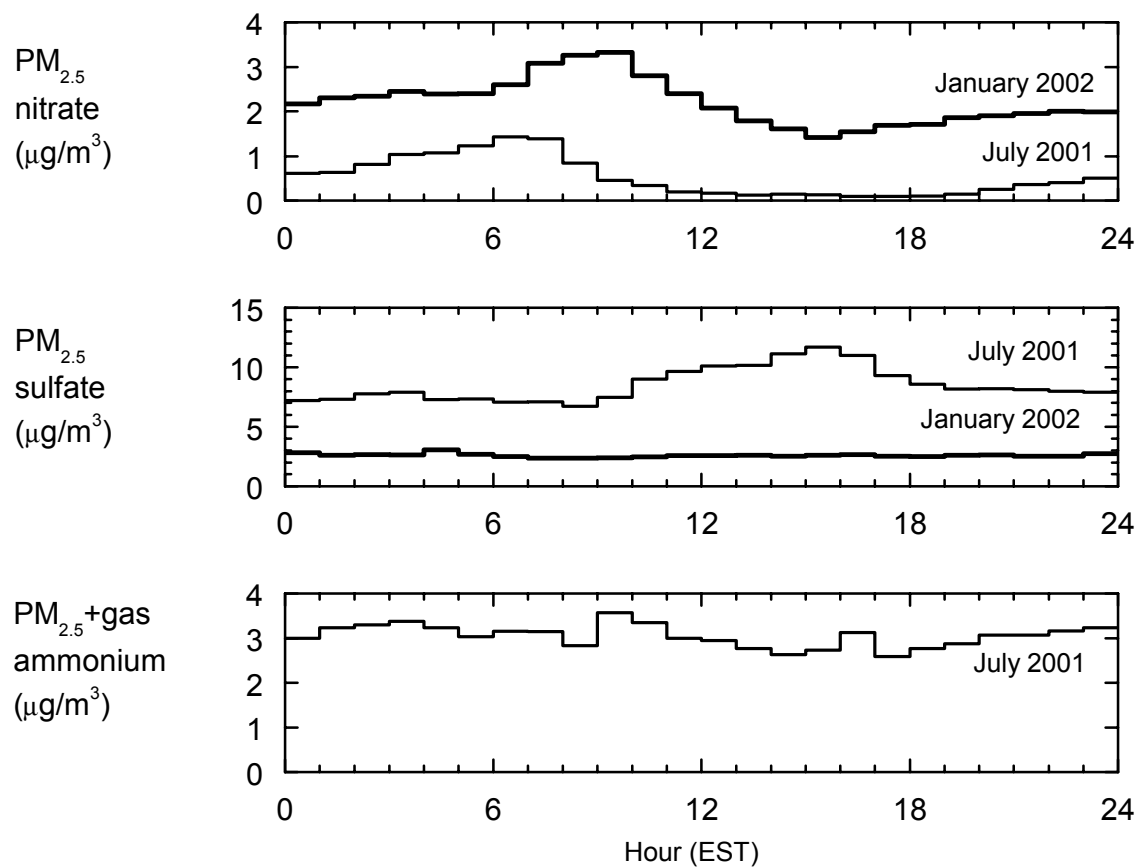


Figure 10. Diurnal variation in PM_{2.5} nitrate, sulfate, and total (PM_{2.5} plus gas) ammonium for July 2001 and January 2002 at the PAQS Supersite. Diurnal values were based on a composite of measurements obtained using the R&P 8400 instruments, the Khylstov steam sampler, and the CMU inorganic sampler.

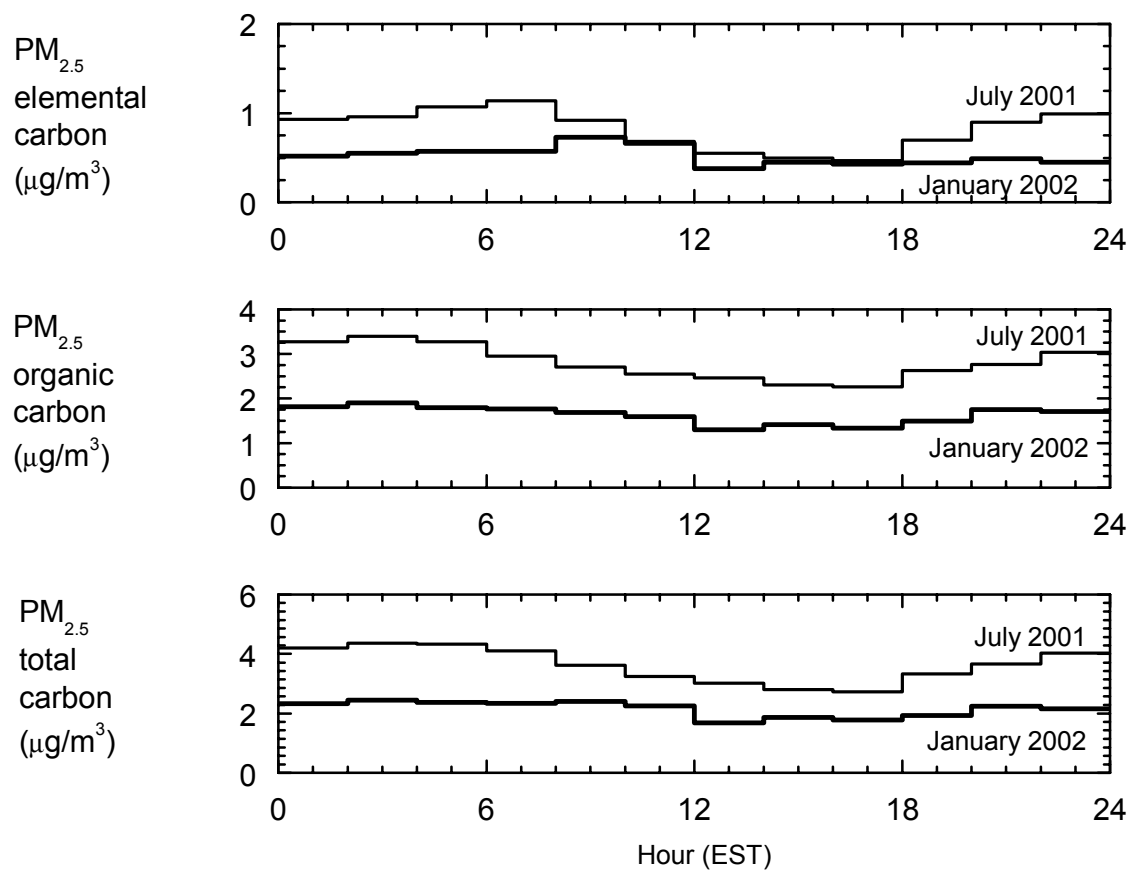


Figure 11. Diurnal variation in PM_{2.5} organic carbon, elemental carbon, and total carbon for July 2001 and January 2002 at the PAQS Supersite. Diurnal values were based on Sunset Labs in-situ carbon analyzer measurements.

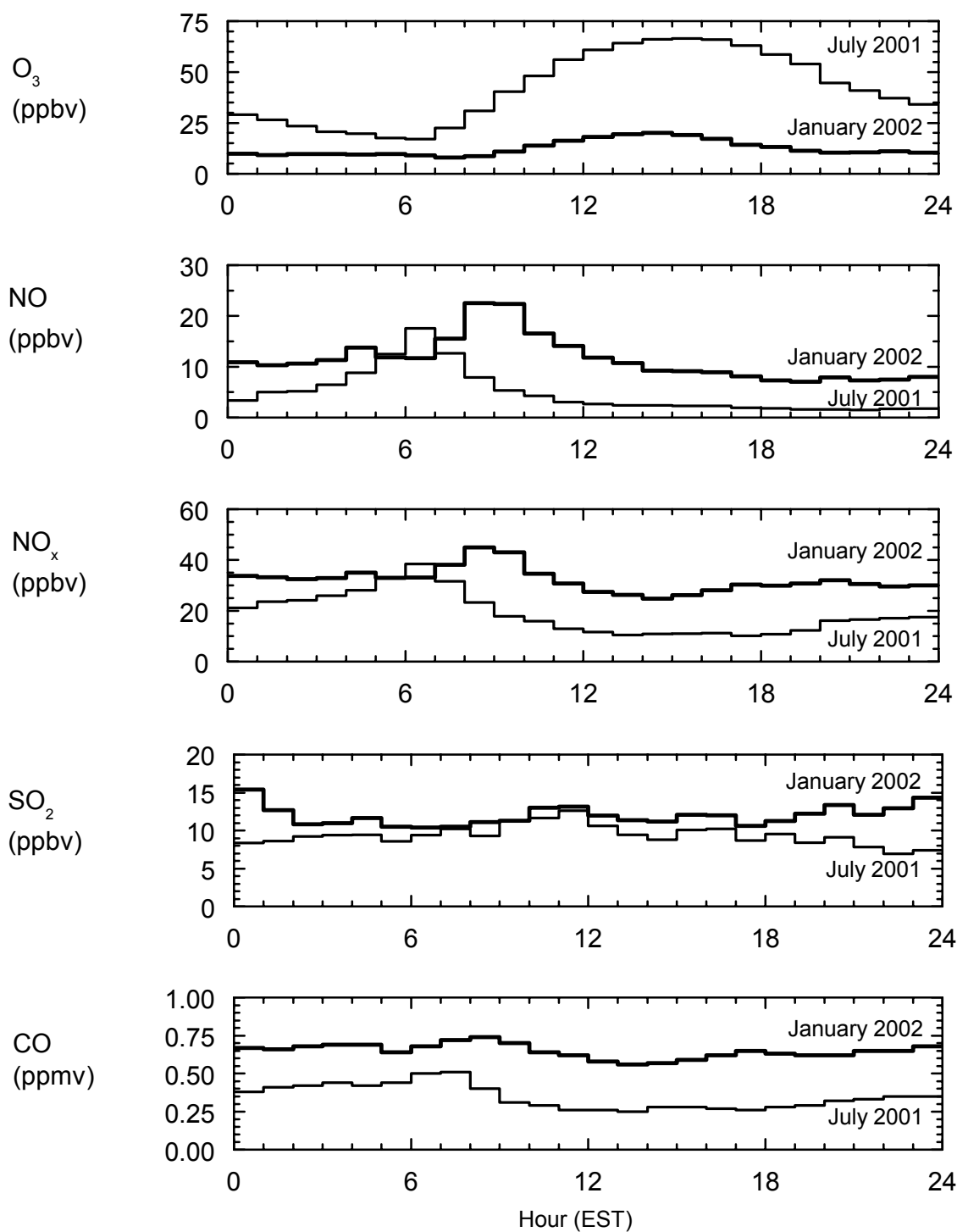


Figure 12. Diurnal variation in gas-phase concentrations of O₃, NO, NO_x, SO₂ and CO for July 2001 and January 2002 at the PAQS Supersite.

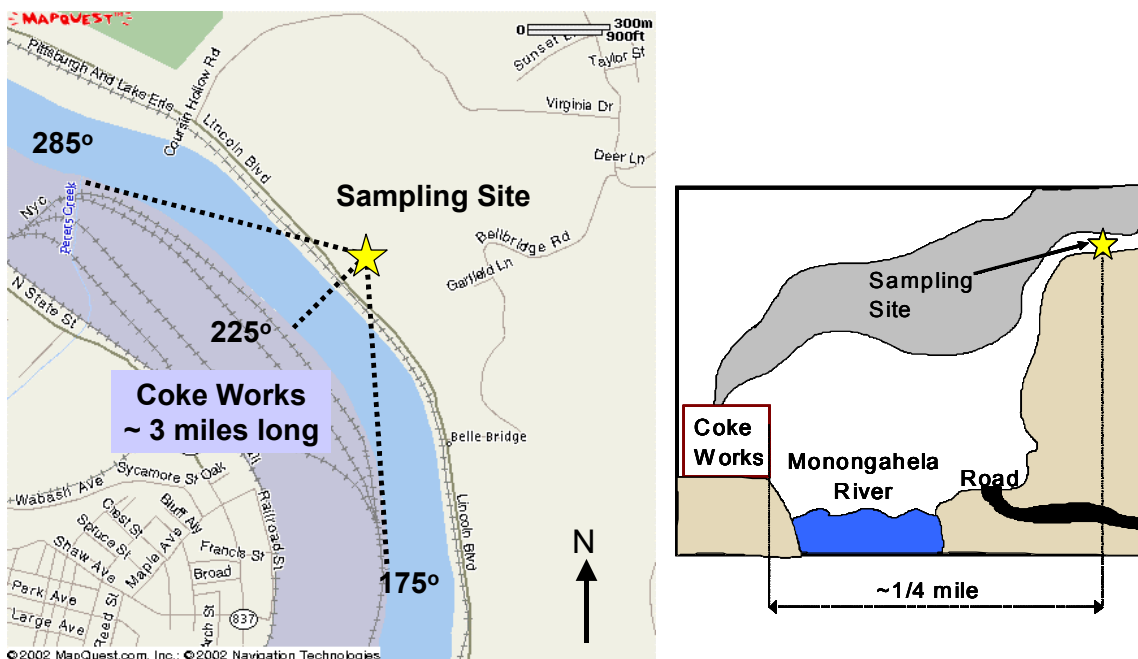


Figure 13. Map and schematic of coke facility and fence line sampling site.

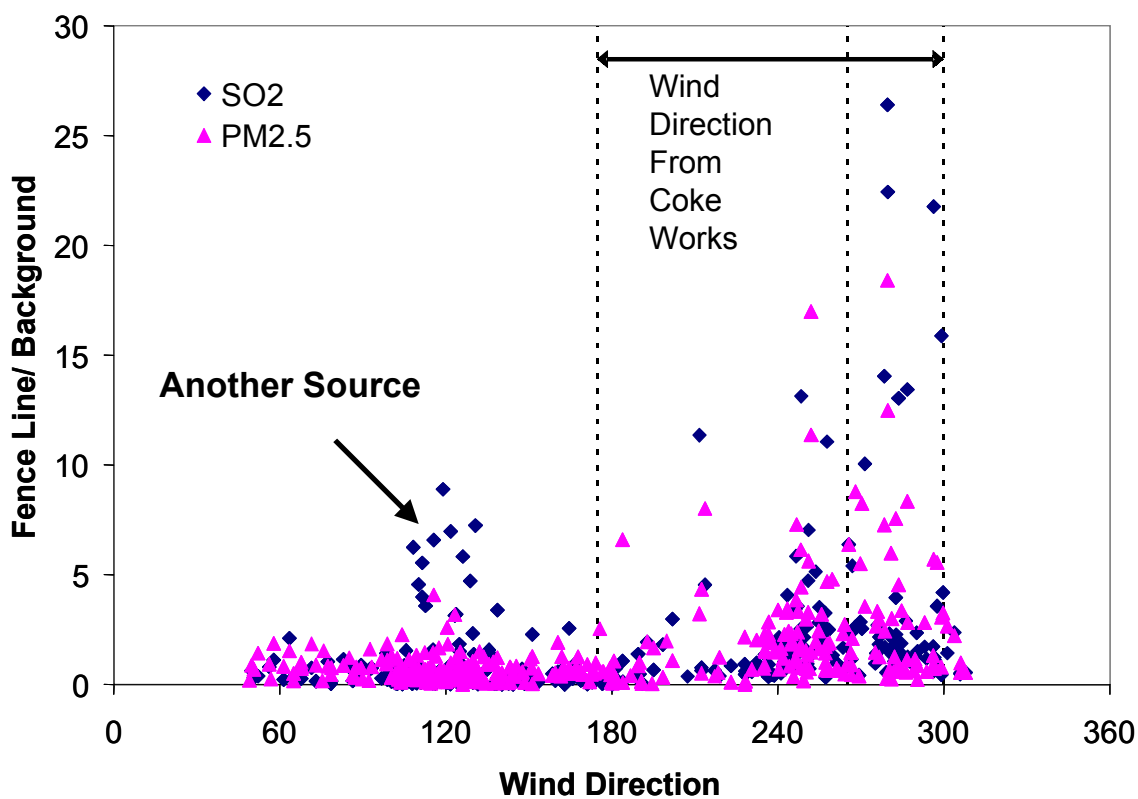


Figure 14. Ratio of the SO₂ and PM_{2.5} concentrations at the fence line site to the background concentrations as a function of wind direction.

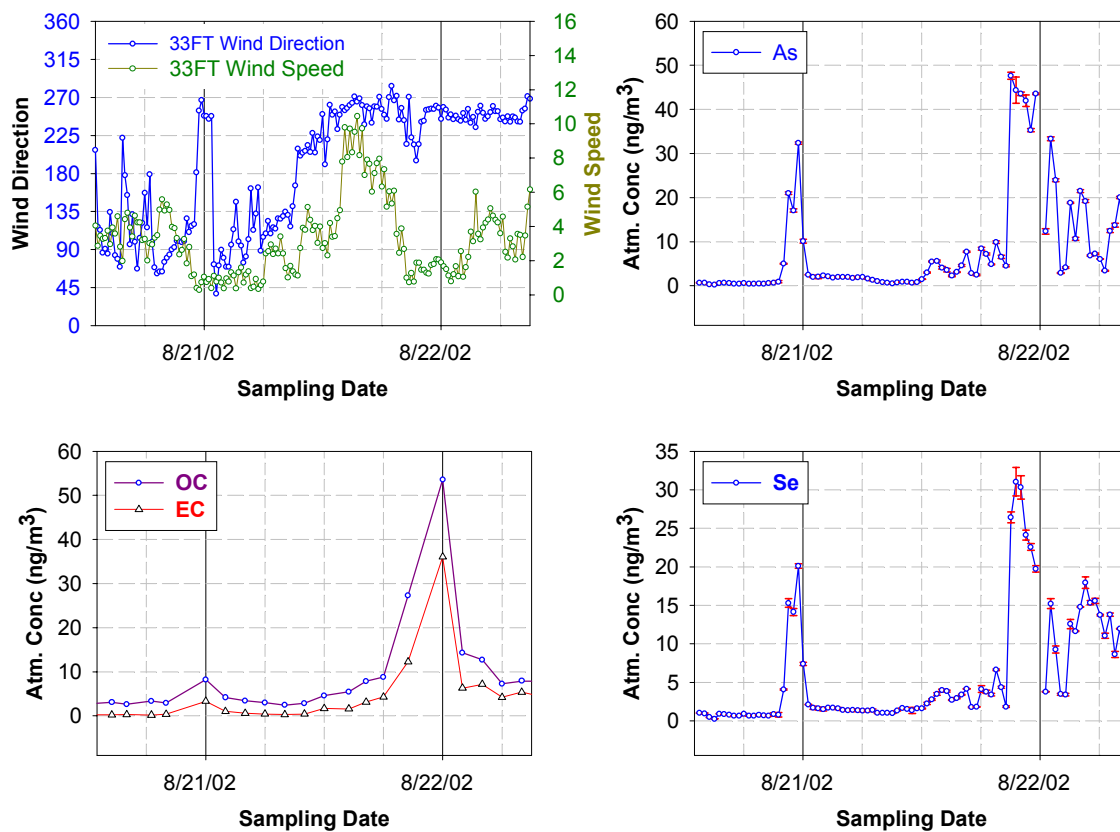


Figure 15. Time series of wind speed, wind direction, PM2.5 Arsenic, PM2.5 OC/EC, and PM2.5 Selenium at fence line site.